

## Preparation and properties of precursor Ba-Ca-Cu-(O,F) thin films deposited from fluorides for superconducting Tl- and Hg- based films

Š. Chromik, M. Jergel, V. Štrbík, Š. Beòàèka,  
Institute of Electrical Engineering, SAS, 842 39 Bratislava, Slovak Republic

C. Falcony  
Departamento de Fisica, CINVESTAV, 07000 México, D.F., México

F. Hanic  
Institute of Measurement Science, SAS, 842 19 Bratislava, Slovak Republic

M. Jergel  
Institute of Physics, Slovak Academy of Sciences, 842 28 Bratislava, Slovak Republic

S. Jimenez  
Laboratorio de Investigation en Materiales, CINVESTAV, Querétaro, Qro 76010, México

J.C.Cheang-Wong, E.Andrade  
Instituto de Fisica, UNAM, 01000México, D.F., México

Precursor Ba-Ca-Cu-(O,F) thin films prepared by thermal evaporation of BaF<sub>2</sub>, CaF<sub>2</sub> and Cu show a good chemical resistance against the atmospheric influence even after a partial defluorination by means of a vacuum annealing with subsequent oxidation. The prepared precursor films were characterized by X-ray diffraction (XRD) analyses and Raman scattering measurements. A possible explanation of the observed properties is presented. According to the XRD measurements performed in the grazing incidence set-up, a polycrystalline cubic BaCuO<sub>2</sub> is the majority phase after defluorination followed by an oxidation process. No peaks belonging to carbides (as a consequence of an atmospheric exposure of samples) were identified. Raman analysis confirmed a presence of another namely CuO phase.

### 1. Introduction

The Ba<sub>2</sub>Ca<sub>2±n</sub>Cu<sub>3</sub>O<sub>7±n+δ</sub> precursors have a great potential for the preparation of high-critical temperature superconducting phases of the M<sub>n</sub>Ba<sub>2</sub>Ca<sub>2±n</sub>Cu<sub>3</sub>O<sub>7±n+m/2+δ</sub> type, where *n* is an atomic index related to the Ca atom, *m* is the formal valency of metal M (M = Tl, Hg, Pb, ... and their combination) and *d* is given by the portion of Cu (III) in Cu. As found by other authors, even the precursors themselves can reach the superconducting state with the T<sub>c</sub> values up to 126 K after a special high temperature treatment of the bulk sample at high pressure<sup>1-3</sup>.

We have used the Ba-Ca-Cu-O precursor thin films prepared by thermal evaporation of BaF<sub>2</sub>, CaF<sub>2</sub> and Cu for preparation of Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>y</sub> (Tl-2212)<sup>4</sup>, and HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>y</sub><sup>5</sup> films. These precursor films showed increased chemical resistance against the influence of an atmospheric surroundings in comparison with the precursor films prepared by rf magnetron sputtering which must always be kept in an argon atmosphere as to minimize their exposure to the moisture and CO<sub>2</sub> from air<sup>6,7</sup>.

It is a purpose of the present paper to show properties of as-evaporated fluorine containing precursors as well as precursors from which the substantial part of fluorine was removed.

### 2. Experimental

BaF<sub>2</sub>, Cu and CaF<sub>2</sub> were sequentially evaporated to produce 0.2 μm thick precursor films with the 2:2:3 cation ratio, on various substrates (single crystal MgO, LaAlO<sub>3</sub>, SrTiO<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> buffered by CeO<sub>2</sub>). During the precursor deposition, the substrate was kept at room temperature followed by an ex-situ vacuum annealing step at the temperature 720 °C in dry oxygen having partial pressure of 10<sup>-2</sup> Pa.

The oxygen partial pressure was gradually increased to the atmospheric one without changing the temperature of the substrate, as to remove a substantial part of fluorine from the BaF<sub>2</sub> and CaF<sub>2</sub> containing precursor film. We prefer this type of fluorine reduction invented by our group<sup>8,9</sup> because this process avoids that more complicated one linked with the use of a wet oxygen. A simple diagram of the annealing process is shown in Fig.1.

The phase composition of all precursor films was measured by the X-ray diffraction in Bragg-Brentano configuration as well as by the grazing incidence method using various grazing angles (0.5, 1.2 and 3.0°), and CuK<sub>α</sub> radiation. The X-ray diffraction was performed on the Siemens D5000 powder diffractometer equipped with interchangeable grazing incidence attachment. The method of the grazing

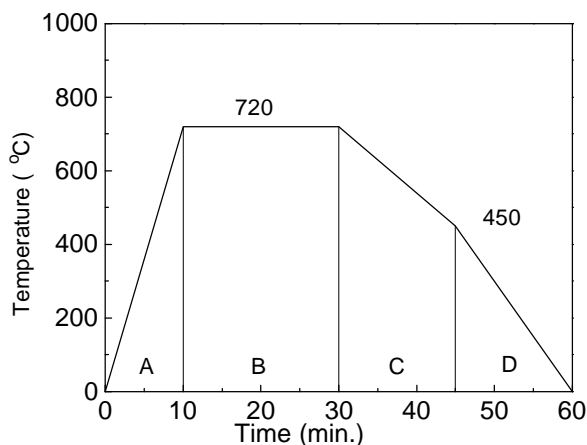


Fig.1. Temperature vs. time of annealing in dry oxygen. The individual time intervals have the following oxygen partial pressures: (A)  $p_{O_2}=10^{-2}$  Pa (B)  $p_{O_2}=10^{-2}$   $10^{-2}$  Pa (C)  $p_{O_2}=10^2$   $10^{-5}$  Pa (D)  $p_{O_2}=10^5$  Pa.

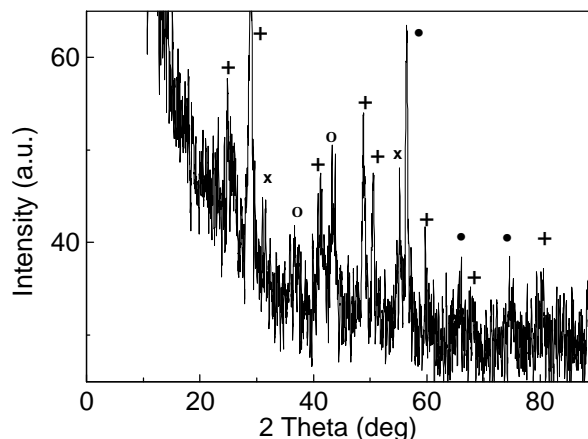


Fig. 2. The X-ray diffraction patterns at grazing incidence of as-evaporated precursor film. The presented phases are marked as: + BaF<sub>2</sub>; x CaF<sub>2</sub>; CuO, o Cu<sub>4</sub>O<sub>3</sub>.

incidence is suitable for measurements of polycrystalline thin films with random orientation of the grains. When the angle of incidence is tuned slightly above the critical angle for the total external reflection, the signal is collected from a near-surface region and contribution of the substrate is then suppressed. Random orientation of the grains gives rise to strongly asymmetrical diffractions. In the presence of a texture with the *c* axis normal to the measured surface (typical for superconducting phases) such diffractions cannot occur and the use of Bragg-Brentano mode is inevitable. Hence, only diffractions from the planes parallel to the film surface are seen.

The unit cell parameters *c* of the tetragonal or orthorhombic phases were evaluated by means of the formula:

$$c = (\lambda / 2 \sin \Delta \vartheta_{21}) (I_1 \cos \vartheta_{0012} - I_2 \cos \vartheta_{0011}),$$

where  $DJ_{21} = J_{0012} - J_{0011}$  is a difference in the applied diffraction angles. For the cubic phase, the following formula was applied:

$$a = (\lambda / 2 \sin \Delta \vartheta_{21}) [(h^2 + k^2 + l^2)^{1/2} \cos \vartheta_1 (h_1^2 + k_1^2 + l_1^2)^{1/2} \cos \vartheta_2],$$

where  $h_i, k_i, l_i$  are selected indices of diffractions, and  $J_i$  are their diffraction angles.

This method, when applied systematically, gives results free from "zero point error", while the "absorption error" is minimized. The Raman scattering measurements were performed in the Dilor micro-Raman system at room temperature. The samples were excited by the 632.8 nm line of a He-Ne laser. A special care was taken to avoid changes in the sample composition by the laser heating effects. To avoid possible errors, the Raman spectra used in this study were taken as average spectra from 30  $\mu$ m line. Some of the investigated precursor films were also thallinated at 850  $^{\circ}$ C for 30 min. in an oxygen flow being placed in a close contact with the crude Tl-Ba-Ca-Cu-O pellet used as a source of thallos ( $Tl_2O$ ) oxide. The R-T (resistance vs. temperature) characteristics of these thallinated precursor films were measured by means of a standard dc four-probe method.

### 3. Results and discussion

The Bragg-Brentano X-ray diffraction patterns provide relatively poor information about the structure of as-evaporated precursor films. The XRD spectra exhibit no BaF<sub>2</sub> or CaF<sub>2</sub> peaks and no evidence about the crystalline character of the films. On the other hand, X-ray spectra taken in the grazing mode (namely at the angle 3 $^{\circ}$ ) showed clearly peaks belonging to BaF<sub>2</sub>, CaF<sub>2</sub> and CuO with various crystallographic orientations, Fig.2.

The consecutive thallination of as-evaporated (i.e. not defluorinated) precursor films yields pure *c*-axis oriented Tl-2212 phase, Fig.3, however, with suppressed values of superconducting transition as it is illustrated in Fig.4, line (a), with  $T_{ons}$ (onset) = 82 K, and  $T_{co}$  (R = 0) = 44 K.

The results of other authors<sup>10</sup> indicate that the relatively high concentration of fluorine in high- $T_c$  superconductors decreases their  $T_c$  possibly by the fluorine occupation of the oxygen positions in the lattice<sup>11</sup>.

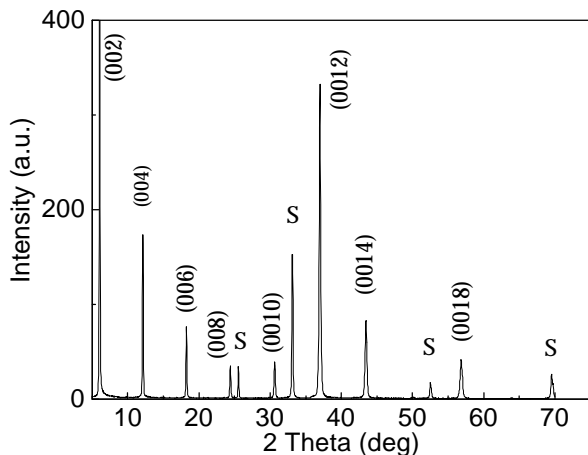


Fig. 3. The X-ray diffraction patterns of the Tl-2212 film prepared by thallination of an as-evaporated precursor film. The identified phases are marked (00) for Tl-2212 and S for sapphire/CeO<sub>2</sub> substrate.

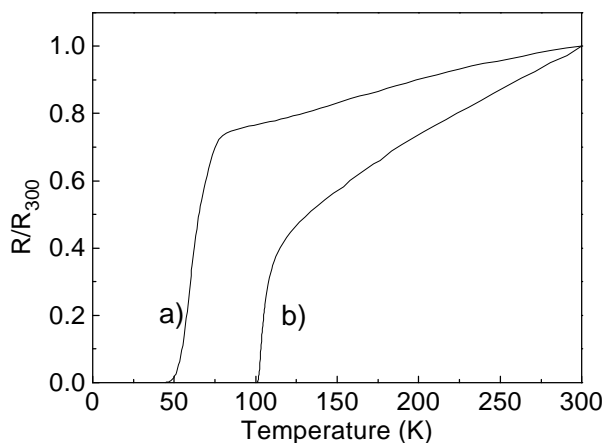


FIG. 4. Comparison of the R-T dependence of TI-2212 film prepared by thallination of as-evaporated precursor film from Fig.3, line (a), and that of another TI-2212 film prepared by thallination of defluorinated precursor film, line (b).

The different *c*-parameter values of thallinated as-evaporated precursor films ( $c=29.2347(4)$  Å) and thallinated defluorinated precursor films ( $c=29.1647(4)$  Å) may also indicate a possible replacement of oxygen by fluorine atoms in the lattice (the ionic radius of F is 1.36 Å, that of O is 1.40 Å). To solve the problem of the  $T_c$  suppression we applied an ex-situ vacuum annealing process in dry oxygen as to remove a substantial part of fluorine<sup>8,9</sup>. The TI-2212 thin films prepared from such defluorinated precursors show superconducting transition typical for this phase, Fig.4, line (b), with  $T_{ons}$  120 K and  $T_{co}$  100 K. We expected that after defluorination the precursor Ba-Ca-Cu-O films would become more sensitive to the atmospheric surroundings similarly as the sputtered precursor films. However, as we found, these annealed precursor films enable us to prepare superconducting TI-2212 films with the same properties, i.e. with  $T_{ons} = 130$  K, and  $T_{co} = 102$  K, even after some months (6) following their defluorination, Fig.5(a).

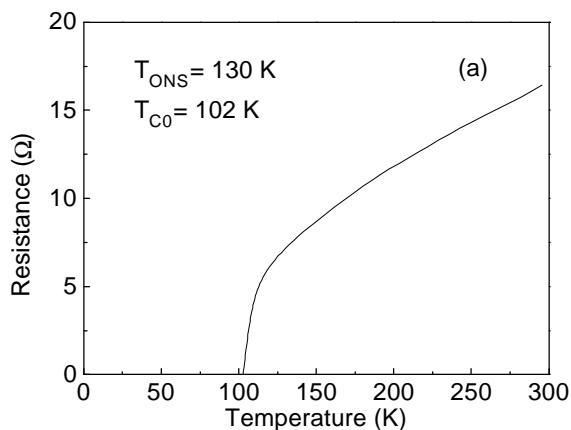


Fig.5(a). The R-T dependence of the TI-2212 film prepared by thallination of a precursor film 6 months after its defluorination.

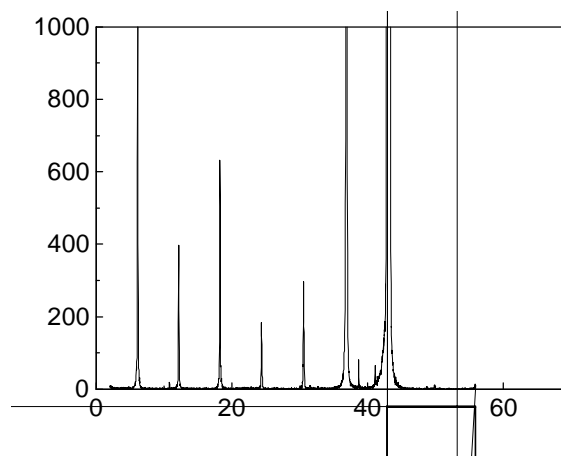


FIG.5(b). The X-ray diffraction patterns of the TI-2212 film prepared by thallination of a precursor film 6 months after its defluorination. The presented phases are marked as: (00) for TI-2212 and S for MgO substrate.

The X-ray data of this particular sample are illustrated in Fig.5(b). Typical Bragg-Brentano and grazing mode X-ray spectra of vacuum and thermally processed precursor film are shown in Fig.6.

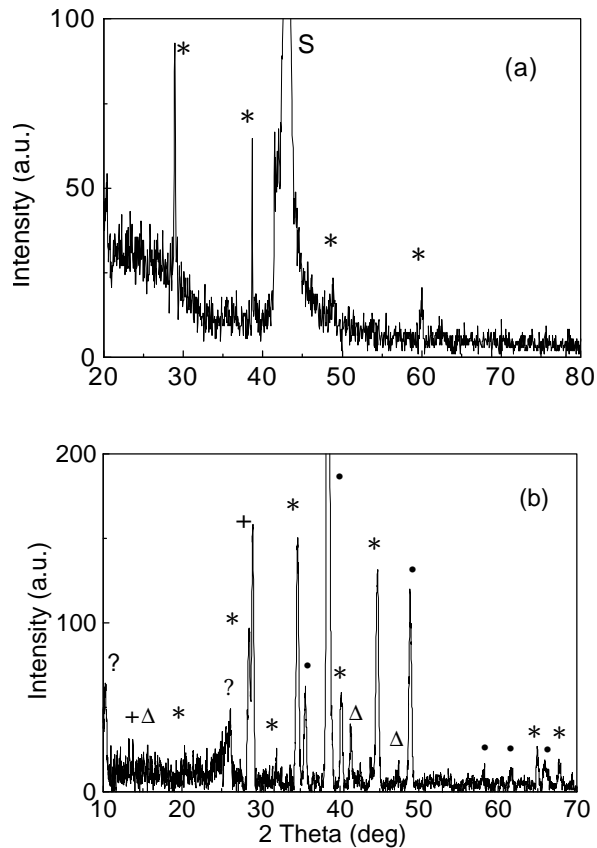


Fig. 6. X-ray diffraction patterns of a vacuum and thermally processed precursor film: (a) Bragg-Brentano, (b) grazing incidence mode. The detected phases are marked as: \*BaCuO<sub>2</sub>, CuO, Δ Ba<sub>4</sub>CaCu<sub>3</sub>O<sub>8+δ</sub>, + BaF<sub>2</sub>, S - MgO substrate, ? unknown phase.

These X-ray analyses confirmed that some traces of  $\text{BaF}_2$  still exist in annealed precursors. While Bragg-Brentano spectra offer not very pronounced peaks belonging mainly to  $\text{BaCuO}_2$ , Fig.6(a), the grazing X-ray patterns indicate more pronounced various phases like  $\text{BaCuO}_2$ ,  $\text{CuO}$ ,  $\text{BaF}_2$ , and also cubic phase  $\text{Ba}_4\text{CaCu}_3\text{O}_{8+\delta}$ . All these detected phases are considered as chemically stable components.

The cubic phase  $\text{Ba}_4\text{CaCu}_3\text{O}_{8+\delta}$  is characterized by the lattice parameter  $a = 8.180(1) \text{ \AA}$  which is comparable with the value of  $a = 8.124(3) \text{ \AA}$ , published by Greaves and Slater<sup>12</sup>. The presence of the  $\text{CuO}$  phase is confirmed also by the Raman scattering measurements, Fig.7. The observed peaks in Raman spectra correspond to the Raman modes of the  $\text{CuO}$  ( $300 \text{ cm}^{-1}$ ,  $350 \text{ cm}^{-1}$  and  $636 \text{ cm}^{-1}$ ) published by Irwin et al<sup>13</sup>. We did not detect any peaks belonging to carbides like  $\text{BaCO}_3$  which may appear as a consequence of an interaction of precursor films with the surrounding atmosphere. Lai et al<sup>14</sup> have prepared Ba-Ca-Cu-O precursor films in a two-step process where as-evaporated Cu- $\text{BaF}_2$  films were preannealed at  $845 \text{ }^\circ\text{C}$  for 3-5 h in pure oxygen in the presence of water vapour as to form stable  $\text{BaCaO}_2$  phase and to eliminate the formation of  $\text{CaCu}_2\text{O}_3$  phase which hinders the growth of the superconducting phase during thallination.

The  $\text{CaF}_2$  component was then added later in the deposition process. It is of interest, that, in spite of the presence of all three components ( $\text{BaF}_2$ ,  $\text{Cu}$  and  $\text{CaF}_2$ ) during our short vacuum pre-annealing (30 min) in dry oxygen, after this processing we observed mainly the  $\text{BaCuO}_2$  and  $\text{CuO}$  phases. We believe that calcium is incorporated into the  $\text{BaCuO}_2$  compound forming thus a solid solution, or it exists in the form of the  $\text{Ba}_4\text{CaCu}_3\text{O}_{8+\delta}$  phase rather than in that of the  $\text{CaCu}_2\text{O}_3$  phase. On the other hand, the amount of a rest of the  $\text{BaF}_2$  component in these precursor films is apparently so low, that it does not suppress the superconducting properties of the film, Fig.4, line (b) and Fig.5 (a).

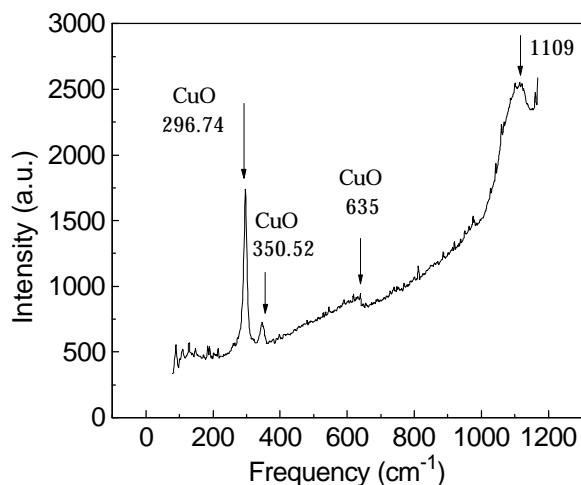


FIG. 7. The room temperature Raman spectra of the annealed (defluorinated) Ba-Ca-Cu-O precursor film.

#### 4. Conclusions

It seems, that the presence of fluorine in the Ba-Ca-Cu-(O,F) precursor films and eventually also in the resulting Tl-based superconducting films plays an important role in two directions.

First, in the precursor films deposited from initial  $\text{BaF}_2$ ,  $\text{CaF}_2$  and  $\text{Cu}$  components, the presence of fluorine ensures the chemical stability in time against the influence of an uncontrolled atmospheric surroundings. However, such as-deposited films with elevated amount of fluorine, when thallinated, they exhibit relatively low  $T_c$ -values, in our case of Tl-2212 films actually below  $50 \text{ K}$ . When the same as-evaporated precursors undergo a thermal heat treatment in a vacuum, a substantial part of fluorine is removed and, upon thallination, the  $T_c$ -values of superconducting Tl-2212 films grown from this type of precursor have increased to the reproducible  $T_c = 100 \text{ K}$ .

Apparently, some „critical“ amount of the fluorine content in the films exists, above which the superconducting properties start to degradate. However, which is of a primary importance, we found that similar good superconducting behaviour of Tl-2212 films may be observed also on films, prepared from precursors thermally processed in vacuum, after 6 months since this treatment. Following both, the Bragg-Brentano as well as the grazing incidence mode X-ray investigations we presume, that the relatively good chemical resistance of precursor films against the atmospheric surroundings might be mainly due to the creation of stable  $\text{BaCuO}_2$ ,  $\text{CuO}$  and  $\text{Ba}_4\text{CaCu}_3\text{O}_{8+\delta}$  phases during the defluorination annealing process.

The second important point is the role of the fluorine presence in the synthesised Tl-based superconducting films, namely its influence upon properties of the grown films. So far not many informations exist in the literature about this subject. Majority of those existing concern the bulk material and some of them are rather contradictory for instance in a case of the  $T_c$ -values, if the fluorine presence increases or decreases these values. It seems, that the knowledge of the precise amount of fluorine in films, both, precursor as well as superconducting ones, may help to clarify this problem.

The work is therefore on the way in our laboratories to quantify the amount of the fluorine content in our films following all stages involved in the superconducting Tl-based film growth, as well as to investigate more in detail the influence of the fluorine presence upon superconducting properties of the prepared Tl-based films.

#### Acknowledgments

This work was supported by the Slovak Grant Agency for Science (Grants No 2/6057/99 and 2/4051/97). The support of CONACyT de Mexico is also greatly appreciated.

## References

- [1] C.W. Chu, Y. Cao, Z.L. Du, L. Gao, K. Ross, I.A. Rusakova, Y.Y. Sun, N.L. Wu and Y.Y. Xue, *Physica C* **282-287**, 57 (1997).
- [2] C.W.Chu, Z.L. Du, Y. Cao, Y.Y. Xue, Y.Y. Sue, I.A. Rusakova, and L. Gao, *Philosophical magazine*, in print
- [3] N.L. Wu, Z.L. Du, Y.Y.Xue, I.A. Rusakova, D.K. Ross, L. Gao, Y. Cao, Y.Y. Sun, C.W. Chu, M. Hervieu and B. Raveau, *Physica C* **315**, 227 (1999).
- [4] Š. Chromik, F. Hanic, M. Jergel, V. Štrbík, and Š. Beòàèka, *Czechoslovak Journal of Physics* **46**, 1517 (1996).
- [5] G. Plesch, Š. Chromik, V. Štrbík, M. Mair, G. Gritzner, Š. Beòàèka, I. Sargánková and A. Buèkuliaková, *Physica C* **307**, 74 (1998).
- [6] F. Foong, B. Bedard, Q.L. Xuand S.H. Liou, *Appl. Phys. Lett.* **68**, 1153 (1996).
- [7] J.D. O'Connor, D. Dew-Hughes, A.P. Bramley, C.R.M. Grovenor, M.J. Goringe and S.M. Morlay, *Appl. Phys. Lett* **69**, 115 (1996).
- [8] Š. Chromik, M. Jergel, F. Hanic, Š. Beòàèka, J. Liday, H. Tollet and C. Creemers, *Physica C* **230**, 82 (1994).
- [9] K. Fröhlich, J. Šouc, Š. Chromik, D. Machajdík and V. Kliment, *Physica C* **202**, 121 (1992).
- [10] N.P. Bansal,A.L. Sandkuhl and D.E. Farrell, *Appl. Phys. Lett.* **52**, 838 (1988).
- [11] N.M. Hamdan, Kh.A. Zig and A.S. Al-Harhi, *Physica C* **314**, 125 (1999).
- [12] C. Graeves and P.R. Slater, *Solid State Commun.* **73**, 629 (1990).
- [13] J.C. Irwin, J. Chrzanowski, T. We, D.J. Lockwood and A. Wold, *Physica C* **166**, 456 (1990).
- [14] H.C. Lai, K.D. Vernon-Parry, J.D. Chern and C.R.M. Grovenor, *Supercond. Sci. Technol.* **4**, 306 (1991).